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Natural and anthropogenic influences on atmospheric Pb-210 deposition and activity in sediments - a review

Inorganic Geochemistry

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Natural and Anthropogenic Influences on Atmospheric Pb-210 Deposition and Activity in Sediments – a review

Dinsley, J. M.; Gowing, C. J. B.; Marriott, A. L.

Ed: Chenery, S. R.; Watts, M. J.

Environmental Science Centre, Keyworth, Nottingham NG12 5GG

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Front cover

Gamma spectrometry instrument at the British Geological Survey's Environmental Science Centre in Keyworth. Gamma Spectrometry is the key method of quantifying Pb-210 activities in sediments.

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British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143 Fax 0115 936 3276

email enquiries@bgs.ac.uk

Environmental Science Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488

email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

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Tel 029 2052 1962 Fax 029 2052 1963

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Department of Enterprise, Trade & Investment, Dundonald House, Upper Newtownards Road, Ballymiscaw, Belfast, BT4 3SB

Tel 028 9038 8462 Fax 028 9038 8461

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Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 Fax 01793 411501

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Foreword

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1 Abstract

The determination of the age of a sediment layer is invaluable for understanding geochemical processes and their time-scales. The application of Pb-210 as a radiometric chronometer has been extensively researched in recent years, being applied to a variety of freshwater, estuarine and marine environments worldwide. The estimation of sedimentation rate changes using Pb-210 dating can also provide valuable information on possible causes for variation in a water body's physiochemical and biological characteristics; making the technique relevant to environmental remediation. However, to reliably draw conclusions based on Pb-210 dating; a comprehensive understanding of the influence that other natural and anthropogenic variables have on Pb-210 is essential.

This literature review summarises the key factors which may influence both unsupported Pb-210 deposition from the atmosphere and the unsupported Pb-210 activity found in sediments. The deposition of unsupported Pb-210 is shown to be predominantly via the rain-out mechanism (within-cloud scavenging) as opposed to wash-out (below cloud), and the suppression or release of Rn-222 exhalation from sediments may also be controlled by surface air temperatures and pressures, which consequently will result in seasonal variations in atmospheric Pb-210 concentrations and Pb-210 deposition. Organic matter (OM), silt and clay content also have an influence on the sediment unsupported Pb-210 activity; thus leading to a general consensus of positive correlation between unsupported Pb-210 activity and the OM, silt or clay content as a result of greater adsorption affinity for Pb-210 and an enhanced specific surface area relative to sand and larger particles. Bioturbation will also impact the unsupported Pb-210 activity in sediments, however mathematical models used to estimate this influence still require further refinement to accurately represent activity variation associated with different species' burrowing techniques and different soil porosities. Anthropogenic influences on sediment unsupported Pb-210 activity may also have been observed i.e. additional Pb-210 from the anthropogenic source, though research on these are limited and further research is advised in assessing the impact of anthropogenic activities such as farming, mining and fossil fuel combustion.

2 Introduction

Lead isotopes are valuable both as chronometers for sediments and rocks via U-Pb or Pb-Pb dating (Andersen 2002; Brennecka et al., 2010; Brévart et al., 1986;) and also as tracers for environmental pollution (Hansmann and Köppel, 2000; Komárek et al., 2008). The termination of three major radioactive decay chains occurs as a result of the production of stable Pb isotopes: the uranium (Pb-206), actinium (Pb-207) and thorium (Pb-208) chains (Thoennessen, 2016).

However, Pb-210, a radioactive isotope with a half-life of approximately 22 years, can also form through the uranium decay chain, and it is believed that Pb-210 can enable geochronologists to determine sedimentation and erosion rate changes spanning up to the last 100 years (Argonne National Laboratory, 2005; DEFRA, 2014; Appleby and Oldfield, 1978).

The inference of sedimentation rate via Pb-210 dating is valuable for environmental remediation and land development planning, as sedimentation rate is a major contributing factor to determining a water body's physical and chemical characteristics. These characteristics will in turn influence the nutrient richness and biological activity of water bodies. Through Pb-210 dating, sedimentation rate changes along a sediment core can be measured and linked to key natural and anthropogenic events which may have degraded local ecological habitats over time (Gąsiorowski, 2008; Tahir et al., 2016). By providing a time-scale through radionuclide dating, geochemical patterns and differences in a sediment core can then be applied to potential causal processes (Shennan et al., 2015).

In recent decades, scientists have been refining and validating the Pb-210 dating method for sediments collected across a wide range of environments including those from marine (Nielson and Asmund, 2008), lacustrine (Begy et al., 2014), estuarine (Cheevaporn and Mokkongpai, 1996), and peat bog environments (Appleby et al., 1997). Refining the dating technique across multiple environments is vital; not only due to differences in dynamicity and sediment deposition sources between environments, but also as our understanding of the ecological impact of different past anthropogenic influences is currently not well understood. Human activities such as construction work, agriculture, mining and petrol burning may either alter sedimentation rates or contribute Pb pollution, which will affect the reliability of Pb-210 dating (Cheevaporn and Mokkongpai, 1996; Yang and Appleby, 2016). Combinations of radiometric dating techniques are also becoming more prevalent within the literature in recent years, with Pb-210 dating being made more robust by the simultaneous measurement of other complementary radio-isotopes such as Cs-137 (Sanders et al., 2006; Sert et al., 2016), Pu-239 and Pu-240 (Liao et al., 2014) and Po-210 (Baskaran, 2011).

Refinement is required as the accuracy of Pb-210 dating is limited by the ability to effectively trace changes in Pb-210 concentrations throughout a sediment core. If natural or anthropogenic variables affect either the atmospheric deposition (or supply) of Pb-210 to sediments, or the sediment Pb-210 activity itself, this will consequently affect the reliability and accuracy of Pb-210 dating. A clearer understanding of the impact of different natural and anthropogenic influences on sediment Pb-210 activities is vital in order to produce accurate chronological estimates for soil and sediment cores.

This report aims to provide a comprehensive overview of multiple, different natural and anthropogenic variables that may influence either atmospheric Pb-210 deposition or the activity of Pb-210 within sediments. Natural variables are explored first, determining how different rainfall mechanisms and seasonal trends may influence Pb-210 deposition. This is then followed by a discussion on how sediment Pb-210 activity may be influenced either by the sediment's characteristics (e.g. organic matter content or soil texture) or by bioturbation from the fauna residing in these sediments. As for the anthropogenic variables, studies covering a range of human activities (i.e. fertiliser production, coal burning, leaded gasoline production) are discussed. Clear gaps where further research should be conducted to determine the true impact of a natural or anthropogenic variable are highlighted throughout this review.

3 The Pb-210 Dating Process

The presence of Pb-210 in sediments occurs via two key pathways (Figure 1), producing either 'supported' or 'unsupported' Pb-210. Firstly, supported Pb-210 is produced by the decay of in-situ Ra-226 within sediments. Supported Pb-210 is produced in secular equilibrium with the precursor members of the uranium decay chain. This secular equilibrium forms as the decay rate of a nuclide is the same as its production rate, so in this case, the decay rate of Pb-210 to form Bi-210 or Hg-206 is equal to the rate of Pb-210 production from Rn-222 decay (Oldfield and Appleby, 1984; Ahmed, 2007).

Contemporaneously, Rn-222 can also degas from soil pores and decay into Pb-210 in the atmosphere. Here, atmospheric Pb-210 can adsorb on to aerosols and then be deposited into soil and sediments (Baskaran, 2011; Begy et al., 2008). This Pb-210 is not present in secular equilibrium and is referred to as 'unsupported' or 'excess' Pb-210, as it cannot be accounted for by the decay of an in-situ parent isotope due to the absence of its precursor isotopes (Appleby and Oldfield, 1978).

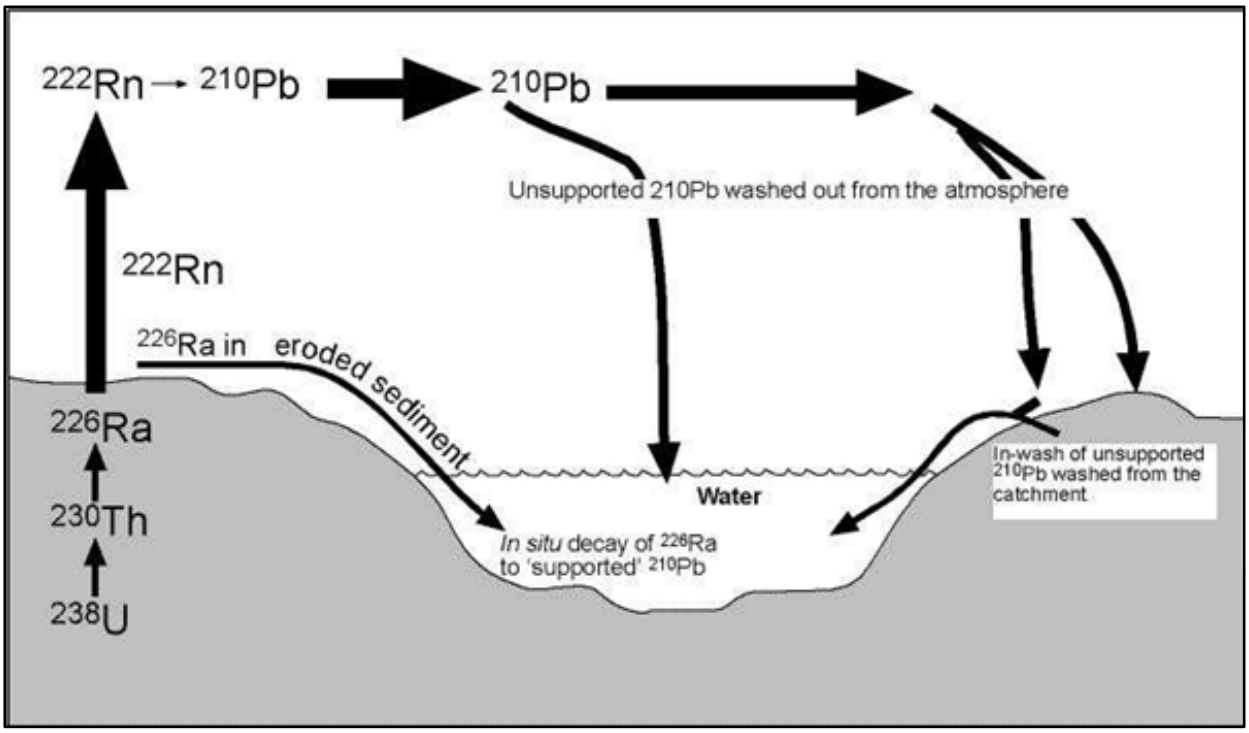


Figure 1. Pathways for Pb-210 to enter water body sediments. Oldfield and Appleby, (1984).

Dating relies on the ability to discriminate between the activity of supported and unsupported Pb-210 within the sediment cores. In the simplest model, the activity of supported Pb-210 within a sediment core is expected to be equal throughout the whole core, assuming that parent nuclide concentrations within the sediment remain constant. On the other hand, the unsupported Pb-210 activity should decrease owing to a longer duration of decay occurring with increasing depth, without replenishment as with sediments close to the surface. Unsupported Pb-210 activity (C_{unsup}) is generally calculated through determination of the total Pb-210 (C_{tot}) and supported Pb-210 (C_{sup}), as indicated by Equation 1 from Zhang et al., (2014):

$$C_{unsup} = C_{tot} - C_{sup} \qquad \text{Equation 1}$$

Ra-226, Pb-214 and Bi-214 sediment activities can also be used as an alternative to supported Pb-210, as the activities of these two isotopes are assumed to be equal to Pb-210 assuming secular equilibrium (Appleby, 1978). Therefore, by subtracting the activity of Ra-226 or Pb-214 from the total Pb-210 activity, the activity of unsupported Pb-210 can be calculated. A worked example adapted from data provided by Tylmann (2004) for the determination of supported and unsupported Pb-210 activity is provided by Appendix A to provide further clarity.

Once the unsupported Pb-210 activity has been calculated at multiple depths, the data can be plotted on a logarithmic scale against the sediment's cumulative dry mass and the mean sedimentation rate can be calculated by measuring the gradient of a least-squares best fit line (Tylmann, 2004). Once the depth (cm), z, and sedimentation rate (cm yr^{-1}), S, are known, Equation 2 can then be used to determine the age (t) of the sediment layer in years (Wilcock, n.d; Appleby and Oldfield, 1978):

$$t = \frac{z}{S} \qquad \text{Equation 2}$$

Alpha and gamma spectrometry are the most commonly used techniques for determining this sediment Pb-210 activity (Walling et al., 1995). Alpha and gamma spectrometry provide easily quantifiable and consistent concentration data for a particular sediment fraction over time, aiding Pb-210 dating. The consistency of the data is also partially due to the limited chemical mobility of Pb-210 under both oxidising and reducing environments (Smith and Schafer, 1984). Despite these benefits however, in order to deduce the activity of unsupported Pb-210, assumptions must be made about either the initial activity of Pb-210 within each sediment layer or the rate of influx of

Pb-210 into each layer (Arnaud, 2002). Therefore, modelling is required to derive a robust dating methodology.

Multiple mathematical models have been developed for Pb-210 dating, with three in particular being widely used within the literature: the Constant Flux - Constant Sedimentation (CFCS); Constant Rate of Supply (CRS) and Constant Initial Activity (CIC) models. All three models are based on the following key assumptions:

1. Pb-210 is removed from both the atmosphere and the water column quickly, to then be sequestered into sediments.
2. Once deposited, the Pb-210 in the sediments is considered to be immobile.
3. The sedimentation process will be uninterrupted.

The optimal model will vary, depending on the environment that it is being used in and the expected constancy of both the Pb-210 influx to sediments and the mass accumulation rate (Le Roux and Marshall, 2011; Shennan et al., 2015).

4 The CFCS, CIC, CRS Models

To fully understand the key components of these models, and to comprehend their differences, a clear understanding of the language is crucial. The *current* unsupported Pb-210 activity is measured for sediment layers at different depths, with activity values used to determine the age of each sediment layer within the core. Once the age of each layer is found, the *initial* unsupported Pb-210 activity of the sediment layer can be extrapolated. This *initial* Pb-210 activity refers to the activity of the unsupported Pb-210 when the layer was first formed (Appleby, 2015).

The original model for Pb-210 dating was the CFCS model – developed through two separate studies by Krishnaswami et al., (1971) and Robbins (1978). This model assumes simplistically that the mass (sediment) accumulation rate, influx of unsupported Pb-210 from the atmosphere, and *initial* activity of Pb-210 within the sediment layer are all constant through time (Shennan et al., 2015). However, there are limited environments which adhere to these assumptions, so this model is rarely selected in more modern studies (Le Roux and Marshall, 2008). As for the two more contemporary models of the CRS and CIC models, these differ in the following ways (Appleby and Oldfield, 1978; Robbins, 1978; Fritz and Fontes, 1986):

The CIC model assumes that the *initial* concentration of Pb-210 remained constant across all sediment layers regardless of changes in mass accumulation rate and depth. In other words if the sedimentation rate changes, the mass of Pb-210 changes proportionally. The excess Pb-210 within each sediment layer ($A(z)$) can be determined as follows (Fritz and Fontes, 1986; González, 2015):

$$A\,(z) = A_0 e^{-\lambda\left(\frac{z}{\omega}\right)t} \qquad \text{Equation 3.1}$$

In which z represents the depth (m) of the sediment layer in the core, t represents the length of time that sedimentation has taken place between the measured layer and the top layer (years), A_0 signifies the Pb-210 activity in the top layer of the core, λ is the Pb-210 decay constant and ω is the annual sedimentation rate (cm yr^{-1}). The radioactive decay constant shows the fraction of atoms that decay per year, and this will vary between isotopes, with the decay constant for Pb-210 being 0.031 yr^{-1}. The radioactive decay constant for Pb-210 of 0.031 yr^{-1} was determined using the natural logarithm of the known half-life for Pb-210 (22.3 years) as below (Corcoran and Kelley, 2006):

$$\lambda = \frac{\ln(2)}{22.26} \qquad \text{Equation 3.2}$$

The annual sedimentation rate of a particular layer can be calculated for use in the CIC formula by dividing the thickness of the layer ($\Delta\chi$) by the estimated time taken to form the sediment (Δt) as shown in Equation 3.3 (González, 2015):

$$\omega = \frac{\Delta\chi}{\Delta t} \qquad \text{Equation 3.3}$$

Once the activity of unsupported Pb-210 within a sediment layer at a specific depth has been calculated using Equation 3.1, an age estimate, t(z), for each layer can be determined by solving the Equation 3.4 (González, 2015):

$$t_{(z)} = \frac{1}{\lambda} ln \frac{A_0}{A_z} \qquad \text{Equation 3.4}$$

However, for the CIC model to work, it is assumed that the sedimentation rate must remain constant, or that a change in the bulk mass accumulation rate will then result in the same magnitude of change to the sediment layer's unsupported Pb-210 concentration – which would then contradict the assumption that the initial unsupported Pb-210 concentration should remain constant between each layer. As a result further research has been conducted within the literature to refine the CRS model, which is better able to account for changes in sedimentation rate or mass accumulation rate (Fritz and Fontes, 1986).

The CRS model is believed to be the most widely used model within the literature for Pb-210 dating (Olid et al., 2012). The CRS model assumes that the rate of supply of unsupported Pb-210 to sediments from the atmosphere at a core location remains constant, irrespective of variations in the mass accumulation rate (accumulation rate for dry mass of sediments or peat soils). This is considered to be a more reliable and realistic model relative to CIC, as the assumption that the initial Pb-210 sediment concentrations were constant for each layer at the time of its formation is highly unlikely to be the case in most deposition environments (Appleby, 2015; González, 2015). The following formula is used to determine the residual Pb-210 inventory ($A\chi$) beneath the layer of age, t, and depth, z (Appleby, 2015):

$$A_\chi = A_0 e^{-\lambda t z} \qquad \text{Equation 4.1}$$

A similar equation to Equation 3.4 can then be used to solve for t, providing an age estimate for the sediment layer (González, 2015):

$$t_{(x)} = \frac{1}{\lambda} ln \frac{A_0}{A_x} \qquad \text{Equation 4.2}$$

As the CRS model uses a cumulative Pb-210 activity with depth, if there is a pause in sedimentation significant errors in the model may creep in.

The selection of which model to use will be dependent on the environment that is being studied, as this will have an impact on the physical, chemical and biological factors which may influence the mass sedimentation rate and sediment profile (Baskaran, 2016). The simpler CIC model has been suggested to be the most appropriate model to use for ageing sediment cores that are collected from a lacustrine environment un-impacted by anthropogenic activities, as sediment accumulation rates normally remain relatively stable over time periods relevant to Pb-210 dating. The CIC model may also be valuable for ice cores, where initial Pb-210 activities will be predominantly determined by the mean annual influx of Pb-210 from local precipitation (Appleby, 2015). However, in an environment with variable mass sedimentation rates (e.g. riverine) or those influenced by bioturbation and organic decay such as a peat bog, the CRS model may be more appropriate (Le Roux and Marshall, 2011; Fritz and Fontes, 1986).

The more sophisticated CRS model has been suggested to be the better option when it is known that the sedimentation rate of an environment is likely to have accelerated owing to anthropogenic influence (Appleby et al., 1979). Fitz and Fontes (1986) demonstrated this in a study of two sediment cores (53C and 104C) from Lake Washington. Whilst both the CIC and CRS models show good agreement in the sedimentation rate between 1800 and 1860, an acceleration in

sedimentation rate between 1860 and 1920 leads to variation between the two models, with the CIC model over-estimating the sedimentation rate by 1.5x that of the CRS model. It is also worth noting that owing to this difference between these two models, the maximum sedimentation rate observed by the CRS model appears to be at approximately 1926 for both the 53C and 104C core, which is approximately 7 years later than the CIC model indicates (Fritz and Fontes, 1986). This difference between the CIC and CRS models can be observed from Figure 2, showing the age-depth profile results for a sediment core collected as part of a study conducted by the British Geological Survey.

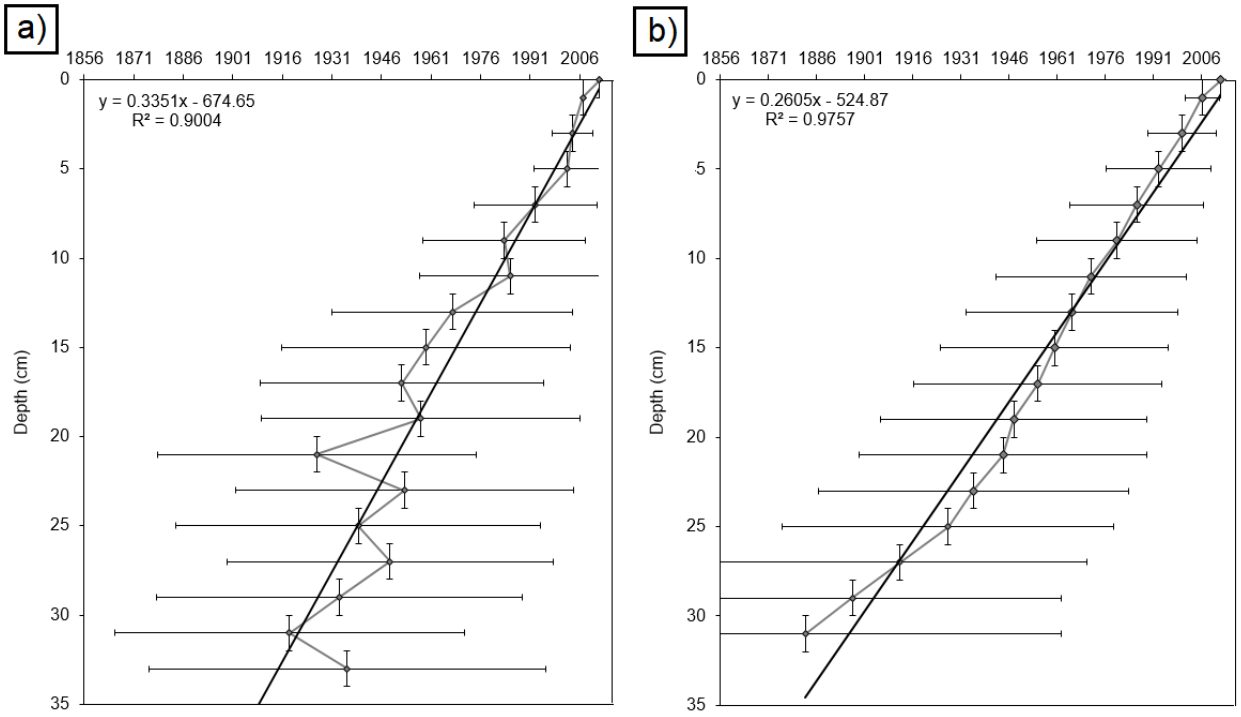


Figure 2. Age-depth profile for a sediment core collected by the British Geological Survey using a) the CIC model and b) the CRS model for sedimentation rate determination.

As the CRS model is likely to be inaccurate where clear gaps in the sediment record appear, and the CIC model is likely to be inaccurate where high levels of sediment mixing have occurred; the decision behind which model is used will invariably require careful consideration and vary with environmental scenario (Lubis, 2006). Alongside selecting the most appropriate model for Pb-210 dating, the influence of environmental factors on atmospheric Pb-210 deposition and sediment Pb-210 activity must also be considered.

5 The Influence of Rainfall on Pb-210 Deposition

Predominant excess Pb-210 production occurs within the troposphere and it can be deposited into sediments through both wet precipitation and dry deposition. As radionuclides are expected to adsorb to aerosols immediately after production in the atmosphere, they can be used as tools to measure aerosol concentration and residence times, allowing the stability of aerosols to be estimated (Tsunogai and Fukuda, 1974).

To understand how rainfall influences atmospheric Pb-210 deposition, a clear understanding of natural precipitation mechanisms is necessary. The deposition of Pb-210 and other atmospheric radionuclides occurs through two main mechanisms: rainout and washout. ‘Rainout’ refers to in-cloud aerosol scavenging, where droplets formed within clouds with absorbed radionuclides, will deposit from the clouds as rainfall. The formation of these rain drops occurs through collision and coalescence of condensation droplets formed around cloud condensation nuclei (CCN), which form progressively larger drops (Beilke and Elshout, 1982; Smithson, et al., 2008). As these rain

drops fall and collide with more aerosols located below the cloud layers, below-cloud scavenging or 'washout' takes place, with rain drops absorbing additional radionuclides from aerosols below the cloud plumes (Scott, 2003).

To determine the wet deposition rate for a rainfall event, the scavenging coefficient (Λ) can be calculated to determine the proportion of radionuclides that have been removed from the cloud plume per unit time (typically measured in units of a fraction per second). Underwood (2001) suggests that at a rainfall rate of 1 mm h^{-1} for 1 µm sized particles, Λ is about 4 x 10^{-5} s^{-1}. However, Λ increases by one order of magnitude if the particle size were to increase from 1 to 10 µm. By using Λ and the known time for the beginning of a rainfall event (t), the concentration of a radionuclide such as Pb-210 still remaining within a cloud plume (Q') under continuous rainfall at a constant rate can be determined using Equation 5 (Scott, 2003):

$$\frac{dQ'}{dt} = -\Lambda Q' \qquad \text{Equation 5}$$

Previous studies indicate that there is a positive relationship between monthly rainfall and Pb-210 deposition (Appleby et al., 2003; Yang and Appleby, 2016). Figure 3 shows the relationship between Pb-210 and Be-7 deposition (Bq m^{-2}) and the monthly rainfall (mm) from Appleby et al., (2013), using data collected at the Blelham Tarn site in the Lake District, Cumbria, UK. This relationship is believed to be owing to more rain being better able to scavenge and deposit a greater quantity of unsupported Pb-210 from the atmosphere (Scott, 2003; Appleby et al., 2013).

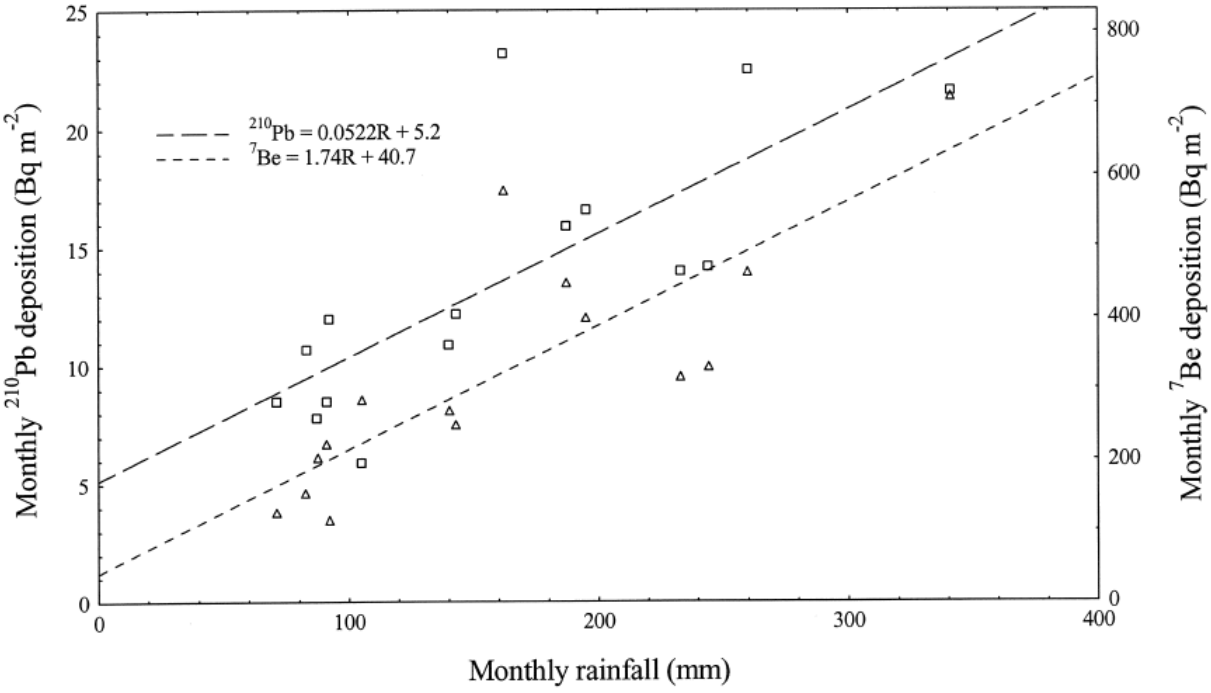


Figure 3. Monthly deposition of Pb-210 (□) and Be-7 (∆) at Blelham Tarn in the English Lake District plotted against monthly rainfall. Regression lines are shown for each radio-nuclide, following a least squares fit analysis. Appleby et al., 2013.

Conversely, Yang and Appleby (2016) also make reference to this relationship when interpreting the Pb-210 activities from rainwater samples collected from Richmond Park, London, UK. However, the study observed greater rainwater Pb-210 activities relative to those collected from Cumbria where precipitation is expected to be greater (Beilke and Elshout, 1982; Yang and Appleby, 2016), with no suggestion provided for the cause of this. However, this conundrum may be owing to more infrequent rainfall in London relative to Cumbria; with the accumulation (and consequently, the rain-out) of excess Pb-210 in the atmosphere being possibly greater in London relative to Cumbria; culminating in higher Pb-210 activities in London's rainwater (Caillet et al., 2001).

Results by Caillet et al., (2001) reinforce the existence of this positive relationship between Pb-210 deposition and rainfall, showing a statistically significant increase in integrated rainfall Pb-210 activity with increasing rainfall ($r^2 = 0.55$, $p<0.001$). The study also measured the difference in rainwater Pb-210 activities between two different groups: an area with low rainfall (Group A) and an area with increasing rainfall over time (Group B). As Group A were shown to have greater Pb-210 rainfall concentrations than Group B, it is likely that washout and dry deposition also play an important role in governing Pb-210 deposition alongside rainout. Heavier rainfall is believed to promote less efficient washout of Pb-210, however at a faster rate, so in the case of torrential rain; the predominant mechanism is rainout (Caillet et al., 2001). The findings of Appleby et al., (2013), Wan (2008), and Yang and Appleby (2016) may indicate that the predominant wet deposition mechanism for Pb-210 is rainout.

6 Seasonal Variation in Pb-210 Deposition

Seasonal variation has also been observed for Pb-210 deposition, with the belief this is owing to changing meteorological conditions. Wan et al., (2008) found that atmospheric Pb-210 concentration was lowest in the late spring and summer months, yet rose during the late autumn/winter months in the Guizhou region of China (**Error! Reference source not found.**a). T his is partly as a result of the rain-out mechanism being more prominent in the Guizhou region in summer (**Error! Reference source not found.**b), although, this may not be the only factor (see Wan et al., 2008).

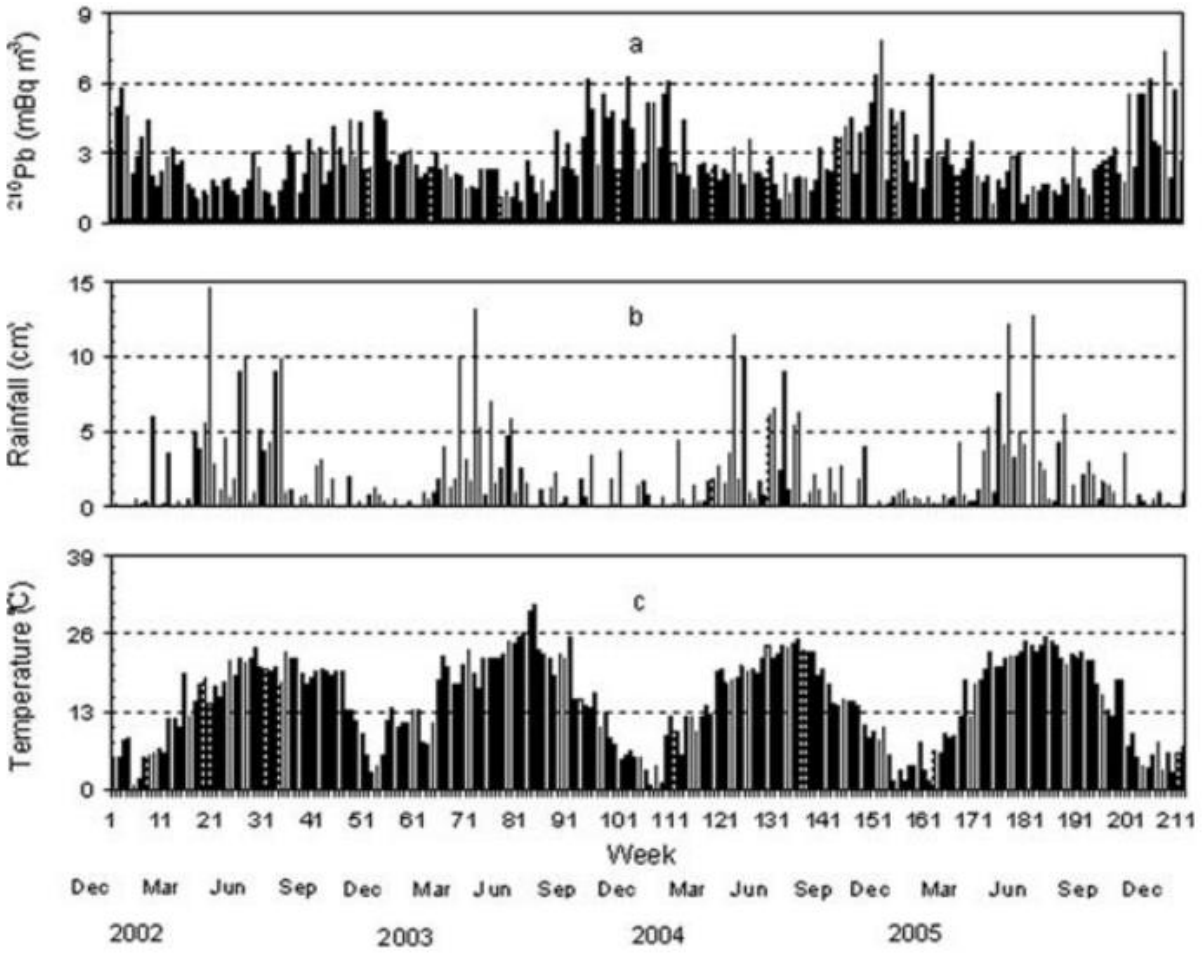


Figure 4. Measurements collected between December 20, 2001 and February 7, 2006 for: (a) weekly surface air Pb-210 concentrations (b) weekly precipitation and (c) weekly mean of air temperatures. Wan et al., 2008.

Increased introduction of oceanic air masses to an area may also result in lower Pb-210 concentrations relative to continental air masses, as greater quantities of radon are able to degas from continental land, forming more Pb-210 (Sugihara et al., n.d.; Fukuda and Tsunogai, 1974; Wan et al., 2008). Therefore in somewhere like the UK, where air-masses may come from either the Atlantic Ocean or continental Europe temporal differences may be enhanced.

The surface air temperature is also believed to influence the seasonal variation in Pb-210, with warm temperatures during summer and colder temperatures in winter being thought to control the exhalation of Rn-222 from local soils (**Error! Reference source not found.**c). In this region, w armer summer temperatures result in a higher pressure atmospheric system that is able to suppress Rn-222 exhalation, resulting in a reduced concentration of atmospheric Rn-222 and consequently, Pb-210. Alongside this, with greater vertical mixing of air masses in the warmer months, the Rn-222 rich air masses will rise from the surface towards the stratosphere, whilst Rn-222 depleted stratospheric air masses will sink towards the troposphere. This can result in a reduced detection of Rn-222 and Pb-210 within the surface air masses during summer (Wan et al. 2008).

In contrast to the results of Wan et al. (2008), Bourcier et al. (2011) found that atmospheric Pb-210 concentrations measured at two sites in France (high and low altitude) were highest in the spring months and lowest in the winter months. Atmospheric Pb-210 concentrations were measured over an annual cycle, and it was found that there was no clear difference between the Pb-210 concentration as a result of the altitude difference between the Puy de Dôme (PdD, 1465 m above sea level) and Opme (660 m above sea level) sites. Bourcier et al., (2011) acknowledges that the results from this study do not follow the wider consensus of lower summer Pb-210 concentrations relative to winter, indicating that the seasonal variation observed for this specific investigation was small and that the difference in rainfall between the spring/summer and winter months for these sites may be the cause for this difference.

7 Influence of Organic Matter Content on Pb-210 Sediment Activity

The influence of organic matter (OM) on re-distributing unsupported Pb-210 is also critical to the dating process. The CRS model assumes that the influx of excess Pb-210 remains constant over time. However this would not be the case if there is a large influx of particulate OM to an aquatic system, which is then able to transfer a larger proportion of unsupported Pb-210 into lake sediments (Wan et al., 2005). By developing our understanding of the influence of OM content on sediment Pb-210 activity, Pb-210 dating models can be further refined and more accurate estimations of sediment chronology can be generated.

Wan et al., (2005) investigated the relationship between the particulate organic carbon content (POC) and the Pb-210 and Cs-137 activities in soil cores collected from Lake Chenghai in China. A significant positive association between unsupported Pb-210 activity and POC was observed ($p=0.002$), whilst a significant negative association was observed between POC and reactive Cs-137 ($p<0.001$). It is possible the positive correlation of Pb-210 is due to how readily scavenged Pb-210 is by organic matter (OM), increasing the ease of adsorption and re-distribution of Pb-210 within a high OM sediment profile (Dörr and Münnich, 1989; Wan et al., 2005).

Miller and Wheeler (2012) have suggested that a greater OM content in the soil would provide a greater food supply for macro and micro fauna and flora, consequently resulting in disruption to the sediment profile via bioturbation. This bioturbation influence will be explored in more depth later on in this report.

Another study by Carvalho (1995) shows agreement with the results from Wan et al., (2005). Carvalho (1995) found that there was a significant correlation between Pb-210 and OM content (%) in sediments collected from the Tagus estuary in Portugal ($r= 0.509$, $n = 67$, $p<0.005$

respectively), with OM content determined using the LOI technique for 6 hours at 450°C. However, both Carvalho (1995) and Wan et al. (2005) did not explain the chemical mechanism that leads to this correlation in great detail.

8 Influence of Soil Texture on Pb-210 Sediment Activity

Soil texture varies spatially, which may result in spatial variation in Pb-210 activity. A previous study by Carvalho (1995) investigated the influence of soil texture on the Pb-210 activity of sediment samples collected from the Tagus river estuary in Portugal. The study was found to be in agreement with Aslani et al., (2005), determining that Pb-210 activity increased inversely with sediment grain size. Carvalho (1995) shows that there is a significant positive correlation ($r = 0.918$, $n = 38$, $p < 0.001$) between the Pb-210 activity and the proportion of the sample that is made up of fine sediment (<63 µm).

He and Walling (1996) also explored this soil texture influence, specifically in relation to the soil particles' specific surface area (SSA) and the distribution coefficient (K_d) for unsupported Pb-210 and Cs-137 adsorption. K_d is defined as the ratio of the radionuclide concentration adsorbed to a unit weight of soil, relative to a unit volume of solution, and the K_d is often used as a measure of the adsorption strength of the nuclide to soil particles. This K_d value is element specific, and can be influenced by the pH, cation exchange capacity and mineralogy of the soil (He and Walling, 1996). He and Walling (1996) found that for both radionuclides, an increase in SSA or K_d led to a rise in radionuclide concentration in soils, with a power function relationship being observed for both soil parameters. This trend is possibly due to an increase in the amount of available adsorption sites on the soil particles with increasing SSA. However, as the concentration of unsupported Pb-210 is greater than that of Cs-137, with differing K_d values, it is possible that the adsorption mechanisms of both radionuclides may differ slightly (He and Walling, 1996).

Overall, there appears to be a consensus in the literature that greater Pb-210 activities are found within sediments with a smaller grain size, and consequently a greater SSA (Carvalho, 1995; He and Walling, 1996; Aslani et al., 2005).

9 Influence of Biological Activity on Pb-210 Sediment Activity

Biological activity may also play a key role in determining sediment or soil Pb-210 activity. One example for this is the influence that bioturbation can have on the Pb-210 activity detected at different depths in sediments. Smith and Schafer (1984) investigated this factor using four marine sediment cores that were collected from along a continental slope: two upper rise cores representing areas of low bioturbation, and a middle slope and lower rise core from areas within an area of high biological mixing. The results of the study showed that the middle and lower cores, where bioturbation was higher, had greater concentrations of Pb-210 at lower depths relative to the upper rise cores, where bioturbation was lower (Figure 5). This occurs as benthic macro fauna are able to construct burrows or displace newer sediments which can then be redistributed further into older strata, transporting excess Pb-210 alongside these newer sediments. Consequently, unsupported Pb-210 activities are greater at larger depths relative to undisturbed sediment profiles.

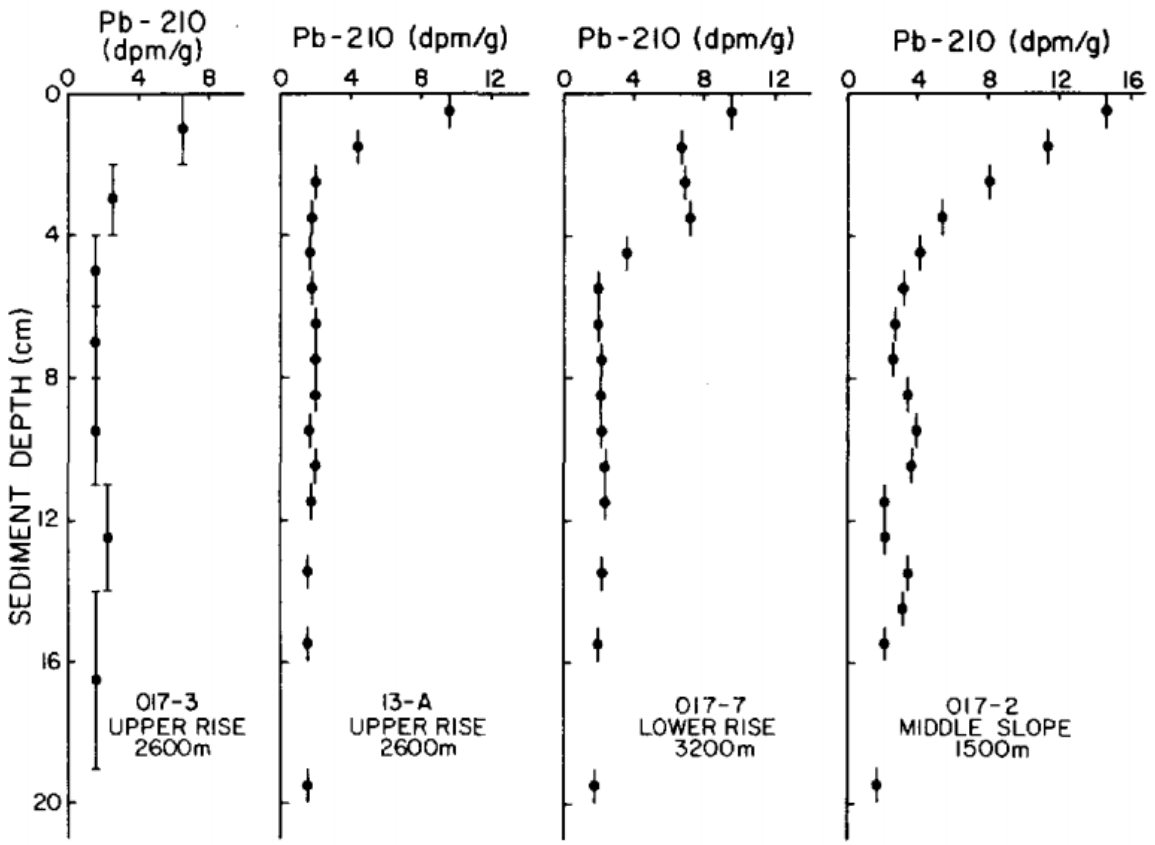


Figure 5. Total Pb-210 activity distribution in four continental slope sediment cores. Cores (017-3 and 13-A) represent the upper rise and are relatively unbioturbated, whilst lower rise and middle slope locations (017-7 and 017-2) exhibit deeper penetration of Pb-210 in sediment cores. Smith and Schafer, (1984).

The influence of bioturbation in sediment cores is often modelled through the calculation of the biodiffusion coefficient, D_b (Miller and Wheeler, 2012). Meysman et al., (2005) describes the concept of biodiffusion as being the 'mathematical model that treats bioturbation as a diffusive process' and it is often linked to Fick's laws of diffusion. Equation 6.1 is adapted in order to link radioactive isotope profiles to bioturbation by utilising D_b, after Miller and Wheeler, (2012):

$$D_b \frac{\delta^2 C}{\delta z^2} - \lambda C = 0 \qquad \text{Equation 6.1}$$

Where $\delta C/\delta z$ is the downwards concentration gradient of Pb-210 in the sediment and λ is the Pb-210 decay constant. Through manipulation of the formula, Pb-210 profiles can be used to calculate the D_b, and so infer the bioturbation effect on sediments (Miller and Wheeler, 2012).

Mulsow and Boudreau (1998) determined that sediment porosity is an important factor to consider for biodiffusion calculations. The study by Mulsow and Boudreau (1998) found that reliable, statistically equivalent D_b values were calculated using models assuming both constant and variable porosity values through the sediment profile, and a change to the porosity gradient will also be likely to result in a change to the sediment Pb-210 activity and mixing. However, as their conclusion was generated based on similar D_b values being generated across only 55% of their Pb-210 plots, there is also an argument to conduct further studies in-situ to refine the current understanding of the relationship between porosity, Pb-210 mixing and bioturbation.

Meysman et al., (2005) refined this investigation into the influence of porosity and drew a similar conclusion to Muslow and Boudrea (1998), indicating that the use of biodiffusion is more complicated than Equation 6.1 implies. As bioturbation occurs, not only will the radioactive isotope gradient be reduced via the mixing, but the porosity gradient of the sediment would also

decrease. The porosity is a key factor to consider when determining the D_b (Kershaw and Woodhead, 1991). Meysman et al., (2005) suggest that the most accurate model to use would be:

$$\frac{\delta}{\delta x}\left[\varphi D_b \frac{\delta C}{\delta x}\right] - \frac{F_{sed}}{\rho}\frac{\delta C}{\delta x} - \phi\lambda C = 0 \qquad \text{Equation 6.2}$$

With x representing the depth, F_{sed} as the constant flux of solid sediment, ρ as the density of the solid phase, φ as the solid volume fraction, and ϕ as the porosity.

There are conflicting studies found in the literature as to whether biodiffusion can be appropriately linked to predicting bioturbation and consequently Pb-210 sediment mixing. Firstly, the influence of porosity may vary depending on whether interphase (mixing of bulk sediment, altering both Pb-210 and porosity profiles) or intraphase (solid materials are mixed, but solid volume fraction and porosity remain unchanged) mixing takes place, and as a result the mathematical equations used will need to vary.

Wheatcroft et al., (1990), as referenced through Miller and Wheeler (2012), also contributes another valuable point in that biodiffusion will not remain steady through-out bioturbation, there will be periods of high and low biological activity. Therefore, trying to form a model that can be used universally under the assumption of a constant D_b may be less reliable. Wheatcroft et al., (1990) suggests that differences in burrowing and sediment displacement techniques used by different organisms will lead to variation in the true biodiffusion impact. A simple example used by Miller and Wheeler (2012) indicates that some animals may generate high horizontal mixing of the top sediment layer, but with limited vertical disruption (e.g. locomotion by benthic bottom-feeders), whilst other animals may burrow deeper into the sediment profile (e.g. worms). Consequently, variation in Pb-210 mixing could also be expected when we model the influence of bioturbation from different species and during pulses of high and low bioturbation activity (Miller and Wheeler, 2012; Wheatcroft, 1992).

An alternative way that biological activity may impact on sediment Pb-210 activity is via the absorption of Pb-210 by organisms prior to its migration into sediments (Tanaka et al., 1983). Tanaka et al., (1983) discovered clear seasonal variation in Th-234 activity when applying a non-steady state model to Japanese seawaters, with the possibility that variation in Pb-210 and Po-210 inventories was also seasonal. The study suggested that the formation of phytoplankton blooms may have been the cause for a minima in the inventories of Th-234, Pb-210 and Po-210 in early spring, as the blooms would absorb these radionuclides from the seawater. As the bloom degrades in summer, the maximum inventories for these nuclides would then be reached, just prior to a secondary algal bloom in autumn. However, whilst Tanaka et al., (1983) provides clear data for this trend being seasonal for Th-234, there is less data available to reliably confirm whether this seasonal relationship exists for either Pb-210 or Po-210. Further investigation into this mechanism of radionuclide uptake by biological organisms is required. If phytoplankton blooms absorb more Pb-210 from the water column, this may lead to Pb-210 not being deposited directly from the atmosphere to sediments. Therefore, the flux of Pb-210 to sediments could become seasonal, coinciding with the bloom formation and degradation.

10 Influence of Anthropogenic Activity on Pb-210 Sediment Activity

Alongside exploring the influence of natural variables; the impact that humans may be having on sediment radionuclide concentrations as a result of land use must also be considered. One example that has been previously studied is phosphate ore extraction (Carvalho, 1995).

Phosphate ore is a valuable resource for the industrial production of fertilisers. Current estimations indicate that approximately 258 Mt of phosphate ore will be mined globally in 2018, a gradual increase up from the 225 Mt that was mined in 2014 (USGS, 2015). However, as rocks rich in phosphate minerals also may contain high quantities of uranium-series radionuclides, the mining and processing of this phosphate ore can result in greater quantities of radionuclides like Pb-210 being liberated into the environment. Wastewater generated during beneficiation of the ores may therefore also contain higher concentrations of radionuclides, which if not responsibly managed can result in enhanced environmental contamination and human exposure risk (EPA, 1993; Carvalho, 1995).

Carvalho (1995) used alpha spectrometry (post-radiochemical separation) to determine the activities of multiple uranium-series radionuclides (including Pb-210) in waste-waters and bulk sediment samples. Activities of up to 1580 Bq kg^{-1} (dry wt.) were observed for the bulk sediment samples within the estuary and this was attributed to the discharge of wastewater from a nearby phosphate fertiliser plant. Greater Pb-210 activities were observed in sediments closer to the point of discharge. As background levels for Pb-210 for sediments were found to be 68 ± 19 Bq kg^{-1} (dry wt.), the study concluded that this large spike in radioactivity was unlikely to be due to other natural factors (Carvalho, 1995).

Another possible anthropogenic source of excess Pb-210 is the combustion of fossil fuels. Fly ash and bottom ash are produced through coal combustion, and both of these may be sources of atmospheric Pb-210 pollution. Whilst fly ash may be released into the atmosphere alongside flue gases as a waste material, disposed bottom ash can also be suspended by the wind or leached into the soil by rain if sent to landfill (Krysiak, 1995). In an effort to minimise this waste, fly ash and bottom ash is often captured and utilised as a concrete additive in the construction industry (World Nuclear Association, 2016). However, fly and bottom ash may also be major contributors of radio-isotopes like Pb-210, Ra-226 and Po-210 to the environment (Glöbel and Andres, 1985). Al-Masri et al., (2014) used gamma spectrometry (HpGe Planar model, Canberra, relative efficiency of 10%) to quantify Pb-210 concentrations in fly and bottom ash, sediment and soil samples collected from the surrounding areas of four heavy oil and natural gas power plants in Syria. Po-210 was also quantified using alpha spectrometry. Concentrations of both radio-isotopes were shown to decrease rapidly with distance from the power plants, with soils and sediments closest to the power plants enhanced by the inclusion of unsupported Pb-210 and Po-210 attached to fly and bottom ash (Al-Masri et al., 2014).

Another example can be observed via the restrictions on leaded gasoline production. The concentration of atmospheric Pb pollution has rapidly decreased subsequently after the 1970s (Figure 6) owing to the introduction of new legislation in Europe and Australia for limiting the quantities of Pb additives that are used in gasoline production, a major contributor to global lead emissions (Yang and Appleby, 2016; von Storch et al., 2003). The need for this legislation arose owing to public concern of the increased risk of blood poisoning and enhanced aggressive and antisocial behaviour being linked to the neuro-toxic effects of lead (Johnson et al., 1995; von Storch et al., 2003; Taylor et al., 2016). As a result of this decline in total atmospheric Pb pollution, coupled with the constant input of Pb-210 over time from radon decay, the ratio of unsupported Pb-210:total Pb has been rising rapidly since the late 1990s (Figure 3; Yang and Appleby, 2016).

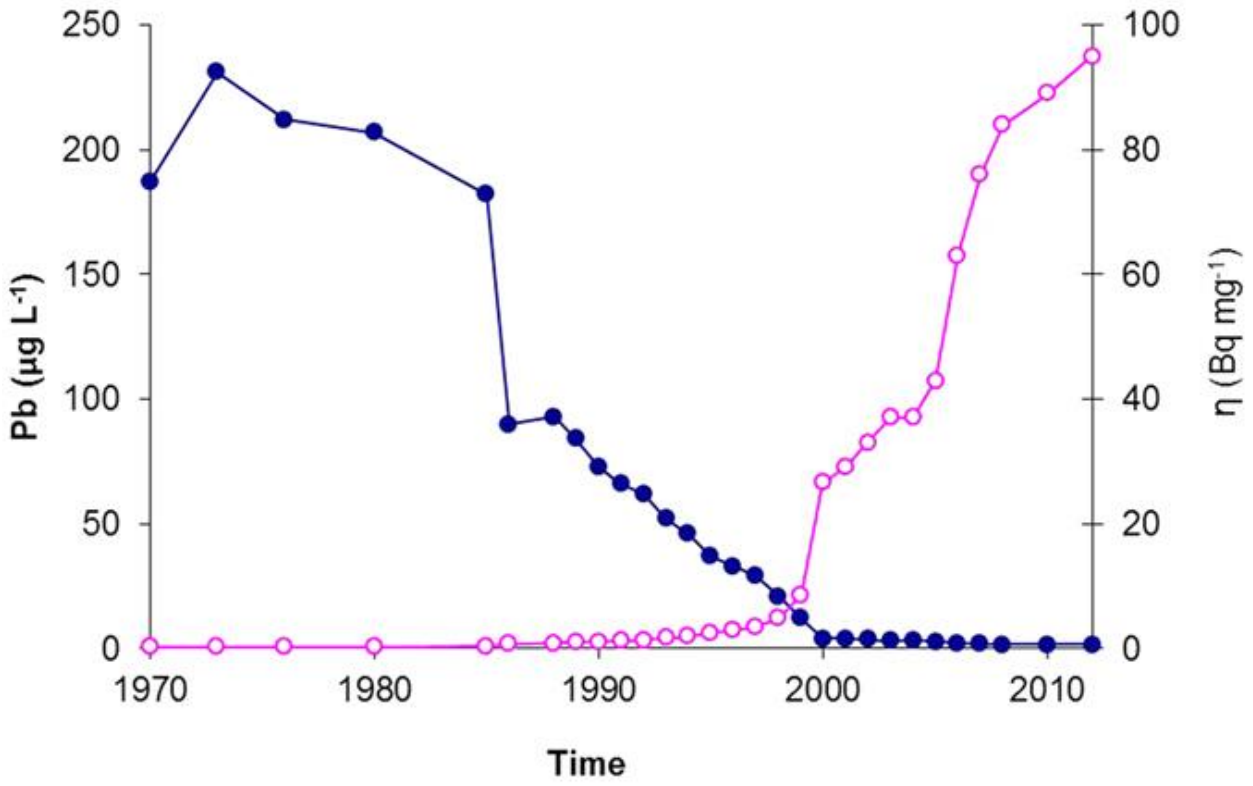


Figure 6. Temporal trends in total atmospheric Pb concentrations (blue filled dots) and in the ratio of unsupported Pb-210: Total Pb, represented by η (pink open dots). Yang and Appleby, 2016.

This ratio is a valuable tool in tracing the contribution of different sources of lead to plants. In order to measure the ratio (η) of unsupported Pb-210: total Pb contributed by contemporary, atmospheric deposition (both natural and anthropogenic input) as opposed to historic deposition (Pb and Pb-210 present within the soil); the following formula was used by Yang and Appleby (2016):

$$F_d = \frac{\eta_p - \eta_s}{\eta_d - \eta_s} \qquad \text{Equation 7}$$

In which F_d represents the fraction of plant Pb originating from contemporary atmospheric fallout, which is calculated using the measurable ratios of Pb-210: total Pb for the plant (η_p), contemporary atmospheric deposition (η_d) and for the soils that feed the plant (η_s). A high Pb-210: total Pb value indicates that a large proportion of the plant's intrinsic lead originated from the relatively recent atmospheric deposition of Pb-210 and Pb, as opposed to intrinsic Pb from the soil (Yang and Appleby, 2016).

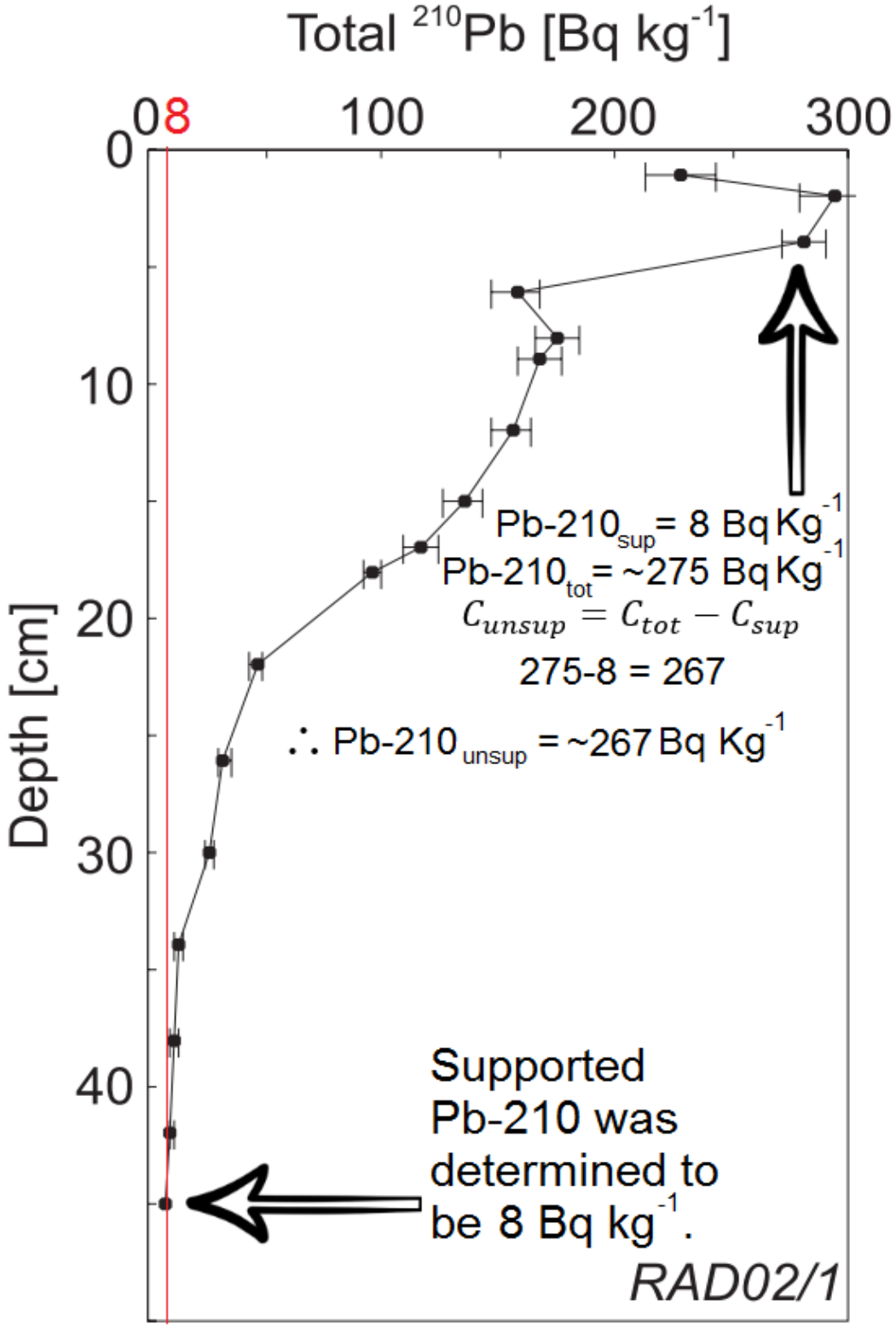
Unfortunately, there are a lack of papers which study the potential anthropogenic influence on Pb-210 sediment activities to date. This is believed to be owing to a combination of the public sensitivity of radiochemistry research and also the difficulty in removing multiple natural confounding variables in order to study the influence of the anthropogenic factors alone. Further research in to this area should be conducted in order to aid decision makers for future pollution reclamation efforts.

11 Conclusion

There are a wide range of natural and anthropogenic variables that can influence both unsupported Pb-210 deposition and unsupported Pb-210 sediment activity. However, current understanding of the chemical mechanisms behind many of these factors is limited and further research is required to fill in these gaps in our knowledge. The rain-out mechanism was found to be the predominant controlling wet deposition method for Pb-210 deposition over wash-out; with a clear positive correlation being found between rainfall and Pb-210 deposition. The sources and temperature of surface air masses may also play a role in the suppression of Rn-222 from the soil and as a result, the atmospheric excess Pb-210 concentration. Soil texture and OM content were also shown to be important factors, with soils containing higher OM, clay and silt contents believed to have a greater unsupported Pb-210 activity owing to a greater specific surface area and affinity for adsorption relative to sand or larger particles. Bioturbation should also be considered and mathematical models designed to link the influence of bioturbation with Pb-210 activity and porosity variation should be further refined. Finally, there is potentially a seasonal pattern for Pb-210 both from a physiochemical perspective (e.g. surface air temperature variations) and from a biological perspective (e.g. phytoplankton blooms).

Appendices

APPENDIX A



Appendix A. Working example of the determination of supported and unsupported Pb-210 activity from total Pb-210 activity in a sediment core. Total Pb-210 activity at the selected point was estimated for demonstrative purposes as no clear value was presented by Tylmann (2004). Adapted from Tylmann, (2004), using data for Core RAD02/1, collected from Lake Raduńskie in Poland. Equation used was taken from Zhang et al., (2014).p

Glossary

Activity (Radiochemistry Context) the amount of disintegrations per unit time per unit mass (e.g. decays per minute per gram). The SI unit for activity is Bq (Wilcock, n.d.). Not to be confused with the definition of 'activity' as a description for 'effective concentration' (Tan, 1998).

Biodiffusion A mathematical model concept which enables bioturbation to be linked to Fick's laws of diffusion (Schulz and Zabel, 2000).

Beneficiation The processing of ores to increase their economic value, often via the removal of gangue (undesired/waste) minerals (Department of Mineral Resources for the Republic of South Africa, 2011).

Sedimentation The transportation and deposition of particles to a water body (Szmytkiewicz and Zalewska, 2014).

Rainout In-cloud aerosol scavenging. Rain droplets are formed within clouds, with radionuclides being deposited as rainfall (Smithson et al., 2008).

Washout Below-cloud scavenging. Rain absorbs radionuclides from aerosols located below the cloud plumes (Scott, 2003).

Soil Texture The relative proportions of clay, silt and sand within a soil (Berry et al., 2007).

Bioturbation The disruption of the sediment layers via biological activity and disturbance (Miller and Wheeler, 2012).

Interphase Mixing The mixing of the bulk sediment fraction in a way where porosity and the solid volume fraction are changed (Meysman et al., 2005).

Intraphase Mixing The mixing of the bulk sediment fraction in a way where porosity and the solid volume fraction are unchanged (Meysman et al., 2005).

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